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(54) Title: POLYETHYLENE BLOW MOLDING COMPOSITION FOR PRODUCING SMALL CONTAINERS

(57) Abstract: The invention relates to a polyethylene composition with multi-modal molecular mass distribution, which is particularly suitable for blow molding of small containers with a volume in the range of from 200 to 5000 cm³ (= ml). The composition has a density in the range of from 0.955 to 0.960 g/cm³ at 23 °C and an MFR_{190/5} in the range from 0.8 to 1.6 dg/min. It comprises from 45 to 55 % by weight of a low-molecular-mass ethylene homopolymer A, from 20 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 20 to 30 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.

Title: Polyethylene blow molding composition for producing small containers

5 The present invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for blow molding of small blow moldings such as containers with a capacity or volume in the range of from 200 to 5000 cm³ (= ml), and to a process for preparing this polyethylene composition in the presence of a catalytic system composed of a Ziegler
10 catalyst and a co-catalyst, by way of a multistage process composed of successive slurry polymerizations. The invention further relates to the small blow moldings produced from the polymer composition by blow molding.

Polyethylene is widely used for producing blow moldings of all sizes requiring a
15 material with particularly high mechanical strength and high stress crack resistance. Another particular advantage of polyethylene is that it also has good chemical resistance and is intrinsically a light-weight material.

EP-A-603,935 has previously described a blow molding composition based on
20 polyethylene and having a bimodal molecular mass distribution, and suitable for the production of moldings with good mechanical properties.

US-A 5,338,589 describes a material with even broader molecular mass distribution, prepared using a high-mileage catalyst known from WO 91/18934,
25 in which the magnesium alcoholate is used in the form of a gel-like suspension. Surprisingly, it has been found that the use of this material in moldings, in particular in pipes, permits simultaneous improvement in properties which are usually contrary correlated in semicrystalline thermoplastics, these being stiffness on the one hand and stress-crack resistance and toughness on the
30 other hand.

However, the known bimodal products in particular have relatively low melt strength during processing. This means that the extruded parison frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being produced, the wall thickness is found to be non-uniform, due to flow of the melt from upper regions into lower regions of the mold.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow molding which shows a further improvement over all of the known materials in processing by blow molding to produce small blow moldings. In particular, the high melt strength of the composition should permit to run an extrusion process without parison disruption over a long time period, and the precisely adjusted swell ratio of the composition should permit an optimization of wall-thickness control.

We have surprisingly found that this objection is achieved by way of a composition as mentioned at the outset, the characterizing features of which are that it comprises from 45 to 55 % by weight of a low-molecular-mass ethylene homopolymer A, from 20 to 35 % by mass of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 20 to 30 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the molding composition.

The invention also relates to a process for preparing this composition in a cascaded slurry polymerization process and to a process for producing small blow moldings such as containers with a capacity (= volume) in the range of from 200 to 5000 cm³ (= ml) and with quite excellent mechanical strength properties.

- The polyethylene composition of the invention has a density in the range of from 0.955 to 0.960 g/cm³ at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small proportions of other 1-olefin monomer units having from 4 to 8 carbon atoms,
- 5 namely from 0.1 to 0.6 % by weight. Examples of these co-monomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene copolymer C also contains an amount of 1-olefins in the range of from 0.5 to 2.5 % by weight of one or more of the above-mentioned co-monomers.
- 10 The pellitized polymer composition of the invention has a melt flow index (ISO 1133) in the range from 0.8 to 1.6 dg/min, expressed in terms of MFI_{190/5}, and a viscosity number VN_{tot} in the range from 280 to 350 cm³/g, measured according to ISO/R 1191 in decalin at 135 °C.
- 15 The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers
- 20 formed in each of the stages of the reaction are therefore as follows:

The viscosity number VN₁ measured on the polymer after the first polymerization stage is identical with the viscosity number VN_A of the low-molecular-mass polyethylene A and according to the invention is in the range of

25 from 70 to 90 cm³/g.

The viscosity number VN₂ measured on the polymer after the second polymerization stage is not equal to VN_B of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be

30 determined by calculation, but rather represents the viscosity number of the

mixture of polymer A and polymer B. According to the invention, VN₂ is in the range of from 150 to 200 cm³/g.

The viscosity number VN₃ measured on the polymer after the third

- 5 polymerization stage is not equal to VN_c of the ultra-high-molecular-mass copolymer C formed in the third polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A, polymer B, and polymer C. According to the invention, VN₃ is in the range of from 260 to 340 cm³/g.

10

The polyethylene is obtained by polymerizing the monomers in slurry in the range from 70 to 90 °C, preferably from 80 to 90 °C, at a pressure in the range from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum

- 15 compound such as triethylaluminum, triisobutylaluminum, alkylaluminum-chlorides or alkylaluminumhydrides. The polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being regulated thereby with the aid of a hydrogen feed.

- 20 The polyethylene composition of the invention may comprise other additives alongside the polyethylene. Examples of these additives are heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds which destroy peroxide, and basic costabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistatics, blowing agents, or a combination of these, in total amounts of from 0 to 50 % by weight, based on the total weight of the mixture.
- 25

The composition of the invention is particularly suitable for the blow molding

- 30 process to produce small blow moldings, by first plastifying the polyethylene

composition in an extruder in the range of from 200 to 250 °C and then extruding it through a die into a mold, where it is cooled and solidified thereby.

The composition of the invention gives particularly good processing behavior in
5 the blow molding process to produce small blow moldings because it has a swell ratio in the range of from 115 to 145 %, and the small blow moldings produced therewith have particularly high mechanical strength because the molding composition of the invention has a notched impact strength (ISO) in the range of from 8 to 14 kJ/m². Its stress-crack resistance (FNCT) is in the range
10 from 8 to 20 h.

The notched impact strength_{ISO} is measured according to ISO 179-1/1eA / DIN 53453 at 23°C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is inserted using an angle of 45°, with a depth of 2 mm and with a notch base
15 radius of 0.25 mm.

The stress-crack resistance of the molding composition of the invention is determined by an internal test method and is given in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and
20 corresponds to ISO/FDIS 16770, which has since come into force. In ethylene glycol as stress-crack-promoting medium at 80°C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced by sawing out three specimens of dimensions 10 x 10 x 90 mm from a pressed
25 plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth is 1.6 mm.

Example 1

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 13.5 mmol/h related to the titanium compound of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the

- 5 operative number 2.2 in the WO, was fed into the first reactor together with 174 mmol/h of triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene, and hydrogen. The amount of ethylene (= 67.2 kg/h) and the amount of hydrogen (= 74 g/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas space of the first reactor were
10 from 20 to 23 % by volume and 66 to 71 % by volume, respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 84 °C.

- 15 The slurry from the first reactor was then transferred into a second reactor, in which the percentage proportion of hydrogen in the gas phase had been reduced to 16 to 20 % by volume, and an amount of 120 g/h of 1-butene was added to this reactor alongside with 46.8 kg/h of ethylene. The amount of hydrogen was reduced by way of intermediate H₂ depressurization. 65 to 70 %
20 by volume of ethylene, 16 to 20 % by volume of hydrogen, and 0.15 to 0.20 % by volume of 1-butene were measured in the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 84 °C.

- 25 The slurry from the second reactor was transferred to the third reactor using further intermediate H₂ depressurization to adjust the amount of hydrogen to 2.0 % by volume in the gas space of the third reactor.

An amount of 540 g/h of 1-butene was added to the third reactor alongside with an amount of 32.1 kg/h of ethylene. A percentage proportion of 81 to 84 % by volume of ethylene, 1.9 to 2.3 % by volume of hydrogen, and 1.2 % by volume of 1-butene was measured in the gas phase of the third reactor, the rest being
5 a mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 84 °C.

The long-term polymerization catalyst activity required for the cascaded process
10 described above was provided by a specifically developed Ziegler catalyst as described in the WO 91/18934 mentioned at the outset. A measure of the usefulness of this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of between 1 to 8 h.

15 The diluent is removed from the polymer slurry leaving the third reactor, and the polymer is dried and then pelletized at a temperature between 220 to 250 °C under specific energy consumption 0.2 to 0.3 kW/h/kg. The polymer powder is stabilized with 0.1 % by weight Ca-stearate, 0.08 % by weight Irganox 1010 and 0.16 % by weight Irgafos 168.

20 Table 1 shown below gives the viscosity numbers and quantitative proportions w_A , w_B , and w_C of polymer A, B, and C for the polyethylene composition prepared in Example 1.

25

Table 1

Example No.	1
w_A [% by weight]	46
w_B [% by weight]	32

W_c [% by weight]	22
VN_1 [cm ³ /g]	75
VN_2 [cm ³ /g]	188
VN_{tot} [cm ³ /g]	317
density [g/cm ³]	0.957
MFI _{190/5} [dg/min]	0.95
SR [%]	142
FNCT [h]	10
NIS _{ISO} [kJ/m ²]	12.3

The abbreviations for physical properties in Table 1 have the following meanings:

- 5 - SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s⁻¹, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.
- 10 - FNCT = stress-crack resistance (Full Notch Creep Test) tested using the internal test method of M. Fleißner, in [h].
- NIS_{ISO} = notched impact strength measured as described in ISO 179-1/1eA / DIN 53453 in [kJ/m²] at 23 °C.

15 Example 2

The preparation of the polymer composition was performed in the same manner as described in Example 1, however, with the difference that the

Ziegler catalyst fed into the first reactor was in an amount of 14 mmol/h, related to the titanium compound instead of 13.5 mmol/h as in Example 1, together with 180 mmol/h of triethylaluminum.

- 5 The amount of ethylene (= 72.8 kg/h) and the amount of hydrogen (= 68 g/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas space of the first reactor were from 21 to 23 % by volume and 67 % by volume, respectively, and the rest was a mix of nitrogen and vaporized diluent.

10

The polymerization in the first reactor was carried out at 85 °C.

- The slurry from the first reactor was then transferred into a second reactor, in which the percentage proportion of hydrogen in the gas phase had been
15 reduced between 6 to 8 % by volume, and an amount of 45 g/h of 1-butene was added to this reactor alongside with 30.8 kg/h of ethylene. The amount of hydrogen was reduced by way of intermediate H₂ depressurization. 79 % by volume of ethylene, 6 to 7 % by volume of hydrogen, and 0.7 % by volume of 1-butene were measured in the gas phase of the second reactor, the rest being
20 a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 82 °C.

- The slurry from the second reactor was transferred to the third reactor using
25 further intermediate H₂ depressurization to adjust the amount of hydrogen to 2.8 % by volume in the gas space of the third reactor.

- An amount of 270 g/h of 1-butene was added to the third reactor alongside with an amount of 36.4 kg/h of ethylene. A percentage proportion of 84 % by volume
30 of ethylene, 2.8 % by volume of hydrogen, and 0.9 % by volume of 1-butene

was measured in the gas phase of the third reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the third reactor was carried out at 85 °C.

5

The polymer leaving the third reactor is then dried, pelletized and stabilized under the same conditions as defined in example 1.

Table 2 as shown below gives more details for the polyethylene composition
10 prepared in example 2:

Table 2

Example No.	2
W _A [% by weight]	52
W _B [% by weight]	22
W _C [% by weight]	26
VN ₁ [cm ³ /g]	85
VN ₂ [cm ³ /g]	194
VN _{tot} [cm ³ /g]	305
density [g/cm ³]	0.958
MFI _{190/5} [dg/min]	1.0
SR [%]	118
FNCT [h]	10
NIS _{Iso} [kJ/m ²]	14

The abbreviations in Table 2 have the same meanings as those in example 1.

We claim

5

1. A polyethylene composition with multimodal molecular mass distribution, which has a density in the range from 0.955 to 0.960 g/cm³ at 23 °C and an MFI_{190/5} in the range from 0.8 to 1.6 dg/min, and which comprises from 45 to 55 % by weight of a low-molecular-mass ethylene homopolymer A, from 20 to 35 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 20 to 30 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the composition.

10

2. A polyethylene composition as claimed in claim 1, wherein the high-

molecular-weight copolymer B contains small proportions of from 0.1 to 0.6 % by weight of co-monomer having from 4 to 8 carbon atoms, based on the weight of copolymer B, and wherein the ultrahigh-molecular-mass ethylene copolymer C contains an amount in the range from 0.5 to 2.5 % by weight of co-monomers, based on the weight of copolymer C.

20

3. A polyethylene composition as claimed in claim 1 or 2, which, as a co-monomer, contains 1-butene, 1-pentene, 1-hexene, 1-octene, 4-

25

methyl-1-pentene, or a mixture of these.

4. A polyethylene composition as claimed in one or more of claims 1 to 3, which has a viscosity number VN_{tot} of from 280 to 350 cm³/g, preferably from 300 to 320 cm³/g, measured to ISO/R 1191 in decalin at 135 °C,

30

5. A polyethylene composition as claimed in one or more of claims 1 to 4, which has a swell ratio in the range from 115 to 145 %, and a notched impact strength (ISO) in the range from 8 to 14 kJ/m², and a stress-crack resistance (FNCT) in the range from 8 to 20 h.
- 10 6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in slurry in a temperature range of from 20 to 120 °C at a pressure in the range of from 0.15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, wherein the molecular mass of the polyethylene prepared in each stage is regulated with the aid of hydrogen.
- 15 7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number VN₁ of the low-molecular-mass polyethylene A is in the range of from 70 to 90 cm³/g.
- 20 8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number VN₂ of the mixture of polymer A and polymer B is in the range of from 150 to 200 cm³/g.
- 25 9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number VN₃ of the mixture of polymer A, polymer B, and polymer C is in the range of from 260 to 340 cm³/g, in particular from 280 to 320 cm³/g.

10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing small blow moldings such as containers with a capacity in the range from 200 to 5000 cm³ (= ml), where the polyethylene composition is first plasticized in an extruder in a temperature range of from 200 to 250 °C and is then extruded through a die into a mold, where it is blown up and then cooled and solidified thereby.

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 45 980 A (ELENAC GMBH) 29 March 2001 (2001-03-29) the whole document	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20 August 1985 (1985-08-20) the whole document	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22 June 1982 (1982-06-22) the whole document	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5 June 2001 (2001-06-05) the whole document	1-10
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 603 935 A (SOLVAY) 29 June 1994 (1994-06-29) cited in the application the whole document -----	1-10

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
DE 19945980	A	29-03-2001	DE AT AU AU BR CA CN DE WO EP JP	19945980 A1 244264 T 769434 B2 7001700 A 0014232 A 2387708 A1 1376170 T 50002772 D1 0123446 A1 1228101 A1 2003510429 T		29-03-2001 15-07-2003 29-01-2004 30-04-2001 04-06-2002 05-04-2001 23-10-2002 07-08-2003 05-04-2001 07-08-2002 18-03-2003
US 4536550	A	20-08-1985	JP JP JP JP JP JP JP JP JP JP JP JP JP JP JP CA DE EP	1012777 B 1612249 C 59196345 A 1012778 B 1612250 C 59196346 A 60036546 A 1012781 B 1612255 C 60036547 A 1218181 A1 3470168 D1 0129312 A1		02-03-1989 30-07-1991 07-11-1984 02-03-1989 30-07-1991 07-11-1984 25-02-1985 02-03-1989 30-07-1991 25-02-1985 17-02-1987 05-05-1988 27-12-1984
US 4336352	A	22-06-1982	JP JP JP BE BR CA DE FR GB IT NL	1282819 C 56032506 A 59010724 B 884866 A1 8005307 A 1138148 A1 3031540 A1 2463791 A1 2056996 A ,B 1193551 B 8004745 A ,C		27-09-1985 02-04-1981 10-03-1984 16-12-1980 04-03-1981 21-12-1982 09-04-1981 27-02-1981 25-03-1981 08-07-1988 26-02-1981
US 6242548	B1	05-06-2001	AU CA EP WO	6044399 A 2372222 A1 1185583 A1 0069969 A1		05-12-2000 23-11-2000 13-03-2002 23-11-2000
EP 0603935	A	29-06-1994	BE AT AU AU BR CZ DE DE EP EP EP ES FI GR HU	1006439 A3 191724 T 670976 B2 5249693 A 9305106 A 9302853 A3 69328345 D1 69328345 T2 1364971 A2 0603935 A1 0940411 A2 2147192 T3 935772 A 3033922 T3 66491 A2		30-08-1994 15-04-2000 08-08-1996 30-06-1994 28-06-1994 13-07-1994 18-05-2000 07-12-2000 26-11-2003 29-06-1994 08-09-1999 01-09-2000 22-06-1994 30-11-2000 28-11-1994

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0603935	A	NO	934729 A	22-06-1994
		PL	301589 A1	27-06-1994
		PT	603935 T	31-10-2000
		US	6344522 B1	05-02-2002
		US	6407185 B1	18-06-2002
		US	6136924 A	24-10-2000
		ZA	9309588 A	11-08-1994